Supplementary Information for:

Conversion of Cyclic Xylose into Xylitol on the Ru, Pt, Pd, Ni, and Rh Catalysts: A Density Functional Theory Study

Shedrack G. Akpea, Sun Hee Choic, * and Hyung Chul Hama,b, *

^a Department of Chemistry and Chemical Engineering, Education and Research Center for Smart Energy and Materials, Inha University, Incheon, 22212, Republic of Korea

^b Program in Smart Digital Engineering, Inha University, Incheon, 22212, Republic of Korea

^c Center for Hydrogen Fuel Cell Research, Korea Institute of Science and Technology, 5 Hwarang-ro 14gil, Seongbuk-gu, Seoul 02792, Republic of Korea

*Corresponding authors:

Prof. Hyung Chul Ham (E-mail: ham.hyungchul@inha.ac.kr; Telephone: +82-32-860-7467, Fax: +82-032-873-0181)

Dr. Sun Hee Choi (E-mail: shchoi@kist.re.kr; Telephone: +82-10-9256-5908; Fax: +82-2-958-5199)

Computational slab Model

Our first principle calculation was conducted in a broader slab, specifically, a 6×4 metal slab due to the large size of the xylose molecule. We discovered that increasing xylose coverage, for example using a 4×4 supercell caused stronger interaction between neighboring atoms, which affects the adsorbate binding, resulting in wrong binding calculations. As a result, a 6×4 model slab with 3 layers was used throughout the study.

Liquid Phase Adsorption of Acyclic Xylose

Although this research focuses on gas-phase xylose hydrogenation, to demonstrate how this reaction will behave in an aqueous environment, we conducted an adsorption study on the RDS's intermediate (acyclic xylose) with the aid of VASPsol, an implicit aqueous model. Similar to the bonding configuration of X_{AC} in the vapor phase, aqueous phase X_{AC} adsorption strength showed a slight reduction across the entire catalyst surface when compared to values obtained in the vapor phase. This result is not surprising given that xylose is not water-soluble. Regardless, the results showed that X_{AC} 's adsorption trend on the catalyst surfaces remained constant in both vapor and water conditions (see Fig. S2), implying that the vapor phase chemistry of this reaction on the investigated catalysts is similar to that in the aqueous phase.



Figure S1. Cylcic xylose adsorption energy trend on a 6×4 supercell slabs with different number of layers.



Figure S2. RDS step intermediate (acyclic xylose) adsorption energy trend in gas and liquid phase media.



Figure S3. Dissociative adsorption of hydrogen molecules (H_2) on Ni (111) (A), Ru (0001), Pd (111) surfaces. (1) and (2) represent adsorbed H_2 before and after geometric optimization (GO).



Figure S4. Investigated conformations of xylose on the studied Surfaces. A, B, C, D, and E represent Ru (0001), Ni (111), Pt (111), Pd (111), and Rh (111), respectively.



Figure S5. Surface intermediate's structures and transition states along the reductive hydrogenation of xylose to xylitol on TS path A on Pt (111) surface. A, B, and C represent Pt (111), Pd (111), and Rh (111), respectively.





Figure S6. Surface intermediate's structures and transition states along the reductive hydrogenation of xylose to xylitol on TS path B1 designated as "Hydro_via_O." A, B, and C represent Pt (111), Pd (111), and Rh (111), respectively.





Figure S7. Surface intermediate's structures and transition states along the reductive hydrogenation of xylose to xylitol on TS path B2 designated as "Hydro_via_C." A, B, and C represent Pt (111), Pd (111), and Rh (111), respectively.